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Anwar A. Bhuiyan
Arkansas Tech University, abhuiyan@atu.edu

S. Kudo
Arkansas Tech University

J. Bartlett
Arkansas Tech University

Synthesis and Characterization of Ruthenium Complexes Containing Chlorophenanthroline and Bipyridine

A.A. Bhuiyan[1,2], S. Kudo[1], and J. Bartlett[1]

[1]*Department of Physical Sciences, Arkansas Tech University, Russellville, AR 72801*

[2]Correspondence: abhuiyan@atu.edu

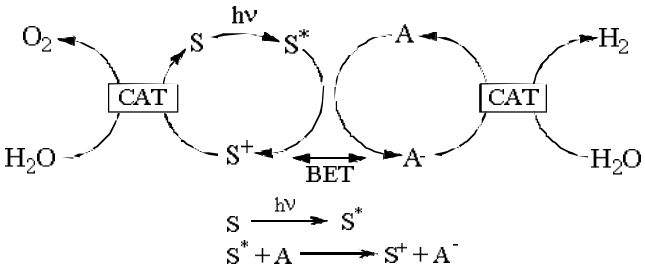
Abstract

The divalent ruthenium polypyridine complexes hold promise as efficient photocatalysts for solar-energy conversion schemes. This paper deals with the synthesis and spectroscopic investigation of ruthenium polypyridine complexes, which may be useful as photosensitizers. The homoleptic ruthenium(II) complex $Ru(Cl\text{-}phen)_3(PF_6)_2$ (where Cl-phen = 5-chloro-1,10-phenanthroline), and heteroleptic ruthenium(II) complexes $Ru(Cl\text{-}phen)_2(bpy)(PF_6)_2$, and $Ru(Cl\text{-}phen)(bpy)_2(PF_6)_2$ (where bpy = 2,2′-bipyridine) have been prepared by following the standard synthetic procedure. Silica and alumina column chromatographies were used to purify the compounds. Mass spectroscopy, nuclear magnetic resonance (nmr) spectroscopy, and elemental analysis were used to confirm the identity and the integrity of the complexes. Absorption and emission spectroscopies in addition to cyclic voltammetry were used to investigate the properties of these complexes. The absorption spectra of all complexes consist of a series of absorption bands in the ultraviolet and visible regions. All three complexes show a strong emission band in the visible region. Cyclic-voltammetric investigations indicate that the chloro substitution either has little impact on the redox properties of the complexes or alters the redox properties in an advantageous manner.

Introduction

Photosynthesis is the process that converts carbon dioxide and water into glucose and oxygen by using the energy from sunlight in the presence of chlorophyll (Lawlor 1993). Photosynthesis is a vital process in maintaining life on Earth. The normal level of oxygen in the atmosphere is maintained by photosynthesis, and all life depends on this process directly or indirectly. Only a very small fraction of the huge amount of available solar energy is used by green plants in photosynthesis. During photosynthesis, green plants convert solar energy into chemical energy by splitting H_2O into H_2. For the last two decades, there has been an intense interest in designing molecular systems that mimic photosynthesis. The strategy has been to design a molecular assembly that will absorb visible light, initiate an electron-transfer process, and ultimately use the solar energy to extract hydrogen for fuel from water (Kalyanasundaram 1987, Parmon and Zamarev 1989).

Hydrogen is one of the most attractive fuels because it does not produce any carbon dioxide or carbon monoxide during combustion, and the only combustion product is water. The energy of a substantial fraction of the sun's spectral output is thermodynamically sufficient to accomplish splitting of H_2O into H_2 and O_2. A synthetic photocatalytic system that can produce hydrogen by the reduction of water is shown in Scheme 1. Several issues such as proper choice of sensitizer, excited-state lifetime, back electron transfer, and suitable redox properties need to be resolved to make Scheme 1 practical. Many attempts have been made (Ramamurthy 1991) to overcome these problems, and the most promising results are obtained by using polypyridine complexes of divalent ruthenium (Jures et al. 1988, Kalyanasundaram 1982).



Scheme 1. Photocatalytic system for splitting of water (S = sensitizer, A = acceptor, BET = back electron transfer, CAT = catalyst).

The long-range goal of our research program is to develop new molecular systems that mimic

photosynthesis. Ruthenium polypyridine complexes have been investigated for use in artificial photosynthesis. It has been documented that ruthenium polypyridine complexes have potential use as efficient photoinitiators in electron-transfer studies (Rillema et al. 1983, Ernst and Kaim 1989, Kawanishi et al. 1989, Lever 1990, Winkler et al. 1982). This has prompted us to further investigate the properties of such complexes. This study has focused on tuning the redox and excited-state properties of ruthenium(II) polypyridine complexes by ligand substitution. It is very difficult to determine what ligand modifications will produce the best combination of excited-state and redox properties. This project is designed to test several ruthenium(II) complexes, homoleptic and heteroleptic with different combinations of ligands, in order to determine how the essential properties are affected.

In this paper, we report efficient synthetic methods for the preparation of $Ru(Cl\text{-}phen)_3(PF_6)_2$, $Ru(Cl\text{-}phen)_2(bpy)(PF_6)_2$, and $Ru(Cl\text{-}phen)(bpy)_2(PF_6)_2$ (where Cl-phen = 5-methyl-1,10-phenanthroline and bpy = 2,2′-bipyridine) complexes (cationic forms are shown in Figure 1). The complexes were purified by column chromatography. The identity and the integrity of the complexes were confirmed by elemental analysis, mass spectroscopy, and nmr spectroscopy. UV-vis absorption and emission spectroscopic methods and cyclic-voltammetric methods were used to investigate the properties of these complexes. Spectroscopic, photophysical, and electrochemical studies document the fact that inherently favorable properties of the parent complexes are not substantially altered by these ligand substitutions.

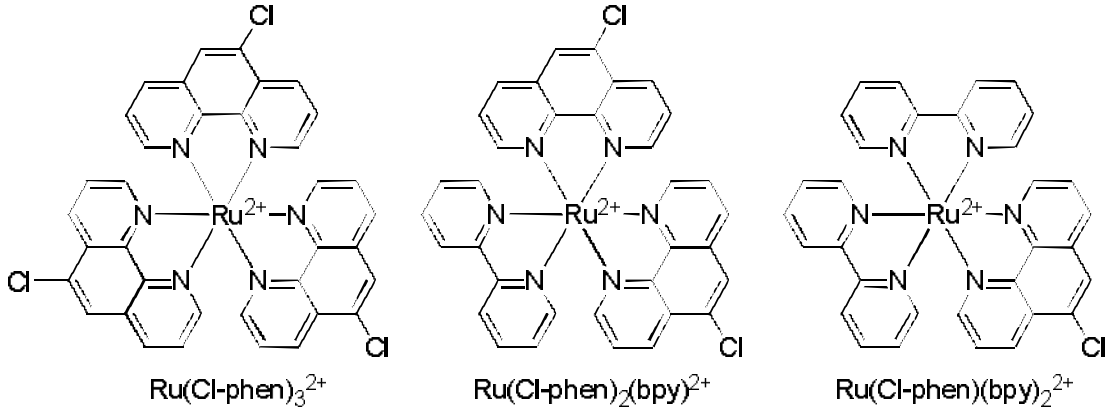


Figure 1. Schematic representation of the prepared complexes.

Materials and Methods

Chemicals

$RuCl_3 \cdot 3H_2O$, 5-chloro-1,10-phenanthroline (Cl-phen), 2,2′-bipyridine (bpy), NH_4PF_6, LiCl, alumina, and high-purity silica gel were purchased from the Aldrich Chemical Company. All the chemicals were used as purchased without further purification. All solvents used were reagent grade or better.

Measurements

Elemental analysis was performed by Columbia Analytical Services, Tucson, AZ. Electrospray ionization mass-spectral (ESI-MS) measurements were performed with a Bruker Esquire LCMS by the Arkansas State Wide Mass Spectromety Facility at University of Arkansas, Fayetteville. All the samples were dissolved in acetonitrile and were injected directly with a flow rate of approximately 50 µL min^{-1} with nitrogen nebulizing gas. ^{1}H-NMR spectra were recorded using a Bruker 400 MHz spectrometer at the University of Arkansas, Fayetteville. Spectra were measured in CD_3CN in δ ppm referenced to tetramethylsilane (Me_4Si). Electronic absorption spectra were obtained with a Shimadzu model UV-2501 PC Uv-vis recording spectrophotometer using a 1-cm quartz cuvette. Spectra were obtained in the absorbance mode. The electronic absorption spectra of all the complexes were measured in acetonitrile solution. The electronic emission spectra were obtained with a PerkinElmer Model LS 55 luminescence spectrometer at 450nm λ_{exc}. The emission spectra of all three complexes were measured in acetonitrile solution at room temperature. Cyclic voltammetry was performed with a CH Instruments Electrochemical Analyzer at the University of Arkansas, Fayetteville.

The working electrode was a 2-mm- diameter platinum-disk electrode, the auxiliary electrode was platinum wire and the reference electrode was a saturated calomel electrode from CH Instruments. Cyclic voltammograms were recorded in 0.1 M $(Bu_4N)(PF_6)$ (tetrabutylammonium hexafluorophosphate) in CH_3CN.

Preparation of Compounds

$Ru(Cl\text{-}Phen)_3(PF_6)$ was prepared by a method previously developed in our laboratory (Bhuiyan et al. 2009); our method is a modification of a method developed by Walker et al. (2004). The reaction involves the substitution of 5-chloro-1,10-phenanthroline for a bipyridine ligand. The compound was prepared by the reaction of $RuCl_3 \cdot 3H_2O$ (1 mmol) and Cl-phen (4 mmol) in 50 mL ethylene glycol under an argon atmosphere. The reaction mixture was refluxed for 4 hours, during which there was a color change from dark black to bright orange. The resulting solution was then cooled to room temperature and filtered. The product was precipitated as a PF_6 salt by adding a saturated solution of aqueous ammonium hexafluorophosphate (NH_4PF_6). This mixture was refrigerated overnight to enhance the precipitation, and the precipitate was collected by vacuum filtration. The precipitate was washed with cold water to remove excess NH_4PF_6, and was finally washed with diethyl ether. After the precipitate was dried in a desiccator, 0.5687 g product was obtained. The crude compound was purified by column chromatography using a silica-gel stationary phase and acetonitrile as an eluent. The first band was collected and added dropwise to diethyl ether, to reprecipitate and 0.3682 g (71% yield) of spectroscopically pure product was obtained.

$Ru(Cl\text{-}phen)_2(bpy)(PF_6)_2$ was prepared by a two-step process. The precursor complex, $Ru(bpy)Cl_4$, was prepared, following a literature method (Krause 1977), by combining $RuCl_3 \cdot 3H_2O$ and bpy (20% excess over one equivalent) in a 1.0 M HCl solution. The mixture was stirred at room temperature to dissolve the solid and was allowed to stand for several days. The resulting black precipitate was vacuum filtered, washed with water, and stored in a desiccator. $Ru(bpy)Cl_4$ was used without further purification.

In the second step, $Ru(bpy)Cl_4$ (0.50 mmol) and Cl-phen (1.50 mmol) were dissolved in 50 mL of an 80/20 ethanol/H_2O mixture. The solution was refluxed for 24 hours under an argon atmosphere. The yellow orange reaction mixture was filtered while hot, and the product was precipitated from the cooled filtrate by addition of a few drops of a saturated aqueous solution of NH_4PF_6. The precipitate was separated by vacuum filtration then washed with cold water and diethyl ether. The brown-yellow product was stored in a desiccator. The crude product was purified by alumina and silica column chromatographies using CH_3CN as an eluent. The yield was 0.3926 g (80% yield).

$Ru(Cl\text{-}phen)(bpy)_2(PF_6)_2$ was also prepared in a two-step process. The precursor complex, cis-$Ru(bpy)_2Cl_2$, was prepared by following the literature method proposed by Sullivan et al. (1978) with a slight modification. $RuCl_3 \cdot 3H_2O$ (1 equivalent), bpy (2 equivalents), and LiCl (0.1 equivalent) were refluxed in 50 mL DMF (dimethyl formamide) for 6-7 hours with constant stirring under argon. After cooling to room temperature, 125 mL of acetone was added into the reaction mixture and stirred for a few minutes. The resulting mixture was placed in a freezer at -5 ^oC overnight. Microcrystalline black precipitate was collected by vacuum filtration. The product was washed several times with cold water and finally with diethyl ether and stored in a desiccator. The identity of the prepared precursor complex was confirmed by absorption spectroscopy.

$Ru(Cl\text{-}phen)(bpy)_2(PF_6)_2$ was prepared from the reaction of $Ru(bpy)_2Cl_2$ (0.5 mmol) and Cl-phen ligand (1.0 mmol). The materials were dissolved in 50 mL H_2O and refluxed 5 hr under argon while stirring. During the reaction, the color of the solution changed from black to brown to blood red. The solution was cooled to room temperature and filtered. Saturated aqueous NH_4PF_6 was added to the filtrate to precipitate the product as a PF_6 salt, and the solution was left in the refrigerator overnight. The orange precipitate was collected by vacuum filtration and washed with cold water and diethyl ether. The product was vacuum dried and placed in a desiccator. The product was purified by silica-gel column with CH_3CN as an eluent. The first band was collected and added dropwise to diethyl ether to reprecipitate. Yield was 0.5180 g (typically ~70% yield).

Results and Discussion

All three complexes, $Ru(Cl\text{-}phen)_3(PF_6)_2$, $Ru(Cl\text{-}phen)_2(bpy)(PF_6)_2$, and $Ru(Cl\text{-}phen)(bpy)_2(PF_6)_2$, were prepared by following the method previously developed in our laboratory (Bhuiyan et al. 2009). The synthetic method for $Ru(Cl\text{-}phen)_3(PF_6)_2$ compound involves only one step, which is based on the pioneering work of Walker and coworkers (2004). This is a very simple, rapid, and convenient method that requires only a slight excess of

ligand. Thin-layer chromatography (TLC) indicated the presence of trace impurities in the complex, which we than removed by column chromatography. The heteroleptic complexes $Ru(Cl\text{-}phen)_2(bpy)(PF_6)_2$ and $Ru(Cl\text{-}phen)(bpy)_2(PF_6)_2$ were prepared by a two-step processes. In the first step, the precursor complexes $Ru(bpy)Cl_4$ and $Ru(bpy)_2Cl_2$ were prepared according to published methods (Krause 1977, Sullivan et al. 1978). Sufficiently pure precursor complexes were obtained and no further purification was necessary. The second step involved the reaction of the previously prepared precursor complexes and additional Cl-phen ligand. This type of procedure is common for mixed-ligand complexes (Bhuiyan et al. 2009, Bhuiyan et al. 2008, Bhuiyan 2008, Bhuiyan and Kincaid 1999). Thin-layer chromatography indicated that all three compounds were slightly contaminated. We used the most common purification method of column chromatography on silica with acetonitrile as an eluent for all three complexes.

The calculated and experimental results of the elemental analysis of all three complexes are given in Table 1. The experimental results are in close agreement with the calculated results for all three complexes, which confirms the identity of the prepared complexes.

The mass spectra of all three complexes are shown in Figure 2. Trace A is for $Ru(Cl\text{-}phen)_3^{2+}$, trace B is for $Ru(Cl\text{-}phen)_2(bpy)^{2+}$, and trace C is for $Ru(Cl\text{-}phen)(bpy)_2^{2+}$. The calculated molar masses for the complexes are 745.0 g/mol [$Ru(Cl\text{-}phen)_3^{2+}$], 686.6 g/mol [$Ru(Cl\text{-}phen)_2(bpy)^{2+}$], and 628.1 g/mol [$Ru(Cl\text{-}phen)(bpy)_2^{2+}$]. The electrospray mass spectrometry of the complexes showed a consistent fragmentation pattern (Figure 2). The experimental isotopic patterns are consistent with the calculated isotopic patterns. Each spectrum showed the molecular-ion peak. The molecular-ion peaks appear at m/z (mass/charge) = 372.8 (trace A), m/z = 343.3 (trace B), and m/z = 313.9 (trace C). From the isotopic patterns, it was confirmed that each ion has an overall charge of 2+, so the experimental molar masses are 745.6 g/mol (trace A), 686.6 g/mol (trace B), and 627.8 g/mol (trace C) for $Ru(Cl\text{-}phen)_3^{2+}$, $Ru(Cl\text{-}phen)_2(bpy)^{2+}$ and $Ru(Cl\text{-}phen)(bpy)_2^{2+}$, respectively. The experimental molar masses are in very good agreement with the calculated molar masses, which confirms the identity and the integrity of the compounds.

The aromatic part of the ^1H NMR spectrum of $Ru(Cl\text{-}phen)_3^{2+}$ is shown in Figure 3. This spectrum exhibits magnetic inequivalence because of the presence of a chloro group on the phenanthroline ligand. The proton peak assignments are made by comparing with the reported spectrum of a cyano-substituted phenanthroline complex (Mellace et al. 2004). H_4 and H_7 are the most affected protons because of the proximity to the electronegative chloro group and are shifted downfield. H_6 has no neighboring protons and therefore appears as a singlet at 8.43 ppm. H_3 and H_8, and H_2 and H_9 are shifted upfield because of nitrogen coordination to the ruthenium(II) ion. As a consequence of coordination and the π back-bonding effect, those protons are strongly shielded and shifted upfield. The integration for each signal is shown at the bottom part of Figure 3, and each of them is consistent with the presence of one proton. The NMR spectra become complicated for mixed-ligand complexes because of the overlap of two ligand bands and are not shown here.

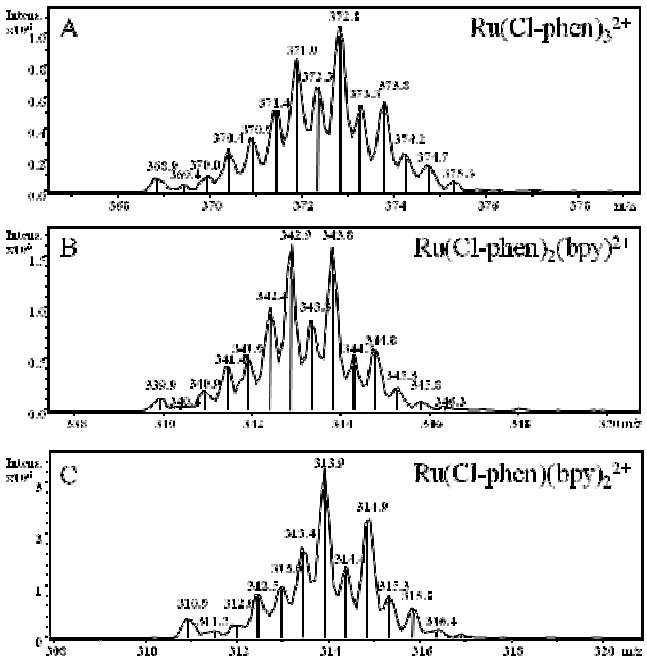


Figure 2. The electrospray mass spectra of the prepared complexes, showing the major fragment cluster. $Ru(Cl\text{-}phen)_3^{2+}$ (trace A); $Ru(Cl\text{-}phen)_2(bpy)^{2+}$ (trace B); and $Ru(Cl\text{-}phen)(bpy)_2^{2+}$ (trace C).

Electronic absorption spectra of all the prepared complexes are shown in Figure 4. The solid-line spectrum is for $Ru(Cl\text{-}phen)_3^{2+}$ (trace A), the dotted line is for $Ru(Cl\text{-}phen)_2(bpy)^{2+}$ (trace B), and the dashed line is for $Ru(Cl\text{-}phen)(bpy)_2^{2+}$ (trace C). The absorption spectra of the complexes are very similar to methyl-substituted complexes previously reported by Bhuiyan et al. (2009). All the spectra consist of a series

Table 1. Comparison of calculated and experimental results of elemental analysis of the prepared complexes.

Formula	$RuC_{36}H_{21}N_6Cl_3P_2F_{12}$			$RuC_{34}H_{22}N_6Cl_2P_2F_{12}$			$RuC_{32}H_{23}N_6ClP_2F_{12}$		
Elements	%C	%H	%N	%C	%H	%N	%C	%H	%N
Calculated	41.78%	2.05%	8.12%	41.82%	2.27%	8.61%	41.87%	2.53%	9.15%
Experimental	41.62%	2.47%	8.56%	41.05%	2.36%	8.30%	41.51%	2.46%	9.12%

of absorption bands in the UV and visible regions. A very strong transition at 266 nm is assigned to a spin-allowed ligand-centered π–π* transition of the Me-phen ligand, and a 285 nm peak is assigned to a π–π* transition of bpy ligand (Kalyanasundaram and Nazeeruddin 1990). $Ru(Cl\text{-}phen)_3^{2+}$ does not contain any bpy ligand, and the 285 nm absorption band is totally absent in the spectrum (trace A). $Ru(Cl\text{-}phen)_2(bpy)^{2+}$ exhibits a 285 nm band as a weak shoulder because of the presence of one bpy ligand (trace B), and $Ru(Cl\text{-}phen)(bpy)_2^{2+}$, with two bpy ligands, exhibits a strong band at 285 nm (trace C). The broad, relatively intense visible band at 450 nm is assigned to a metal-to-ligand charge-transfer (MLCT) transition by comparing with other ruthenium(II) polypyridine complexes (Denti et al. 1990). The higher-energy shoulder observed is assigned to a second MLCT transition.

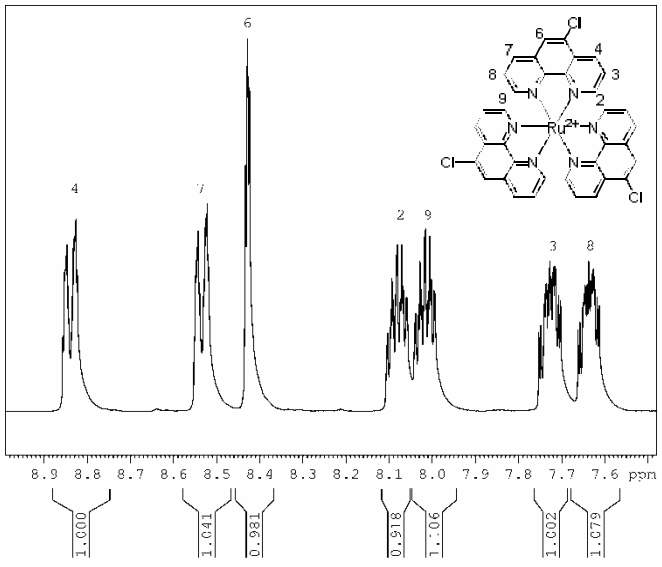


Figure 3. ^1H NMR spectrum of $Ru(Cl\text{-}phen)_3^{2+}$ in the aromatic region between δ 7.5 ppm and 9.0 ppm in CD_3CN (TMS reference)

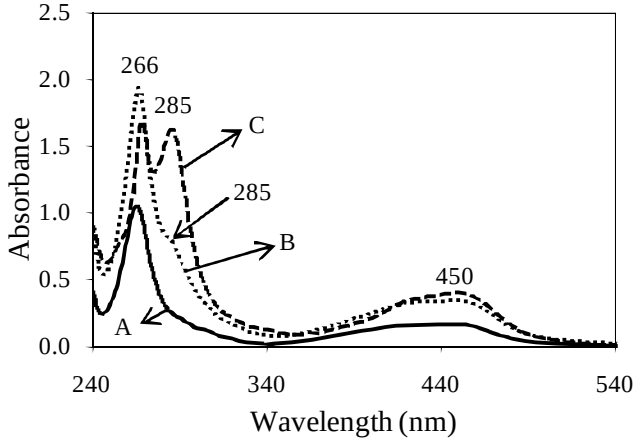


Figure 4. Electronic absorption spectra of the prepared complexes: $Ru(Cl\text{-}phen)_3^{2+}$ (trace A); $Ru(Cl\text{-}phen)_2(bpy)^{2+}$ (trace B); and $Ru(Cl\text{-}phen)(bpy)_2^{2+}$ (trace C).

The room-temperature emission spectra of all the complexes are shown in Figure 5. The excitation wavelength was determined by scanning the excitation spectra at a fixed emission wavelength. The excitation wavelength is 450 nm for all three complexes. The solid line is for $Ru(Cl\text{-}phen)_3^{2+}$ (trace A), the dotted line is for $Ru(Cl\text{-}phen)_2(bpy)^{2+}$ (trace B), and the dashed line is for $Ru(Cl\text{-}phen)(bpy)_2^{2+}$ (trace C). The electronic emission spectra of the complexes exhibit strong emission bands at 587 nm for $Ru(Cl\text{-}phen)_3^{2+}$, at 590 nm for $Ru(Cl\text{-}phen)_2(bpy)^{2+}$, and at 597 nm for $(Ru(Cl\text{-}phen)(bpy)_2^{2+}$. All three complexes exhibit a single emission band, which confirms the purity of the prepared complexes. The emission spectra of the complexes are very similar to methyl-substituted complexes previously reported by Bhuiyan et al. (2009). As for other polypyridine complexes of Ru(II), these luminescence bands have been assigned as the phosphorescent process ^3MLCT (triplet metal-to-ligand charge transfer) → ^1GS (singlet ground state) (Lytle and Hercules 1969, Bhuiyan and Kincaid 2001). The emission maxima are red shifted by 3 nm with the addition of one bpy ligand, and 7 nm with the addition

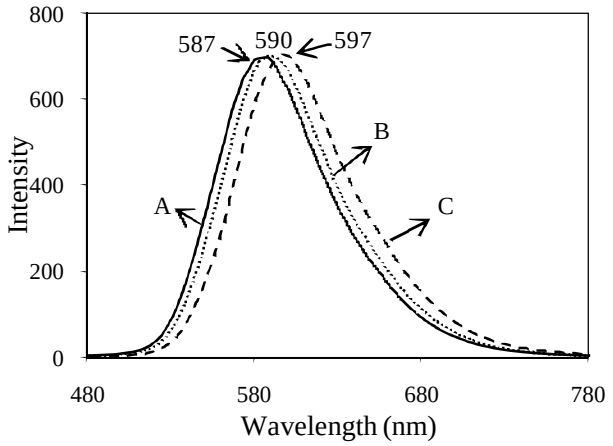


Figure 5. Electronic emission spectra of the prepared complexes: $Ru(Cl\text{-}phen)_3^{2+}$ (trace A); $Ru(Cl\text{-}phen)_2(bpy)^{2+}$ (trace B); and $Ru(Cl\text{-}phen)(bpy)_2^{2+}$ (trace C).

of another bpy ligand. This observation is consistent with the previously reported spectra of similar ruthenium(II) polypyridine complexes (Bhuiyan et al. 2009).

Cyclic voltammograms of all the prepared complexes are shown in Figure 6. The solid line is for $Ru(Cl\text{-}phen)_3^{2+}$ (trace A), the dotted line is for $Ru(Cl\text{-}phen)_2(bpy)^{2+}$ (trace B), and the dashed line is for $Ru(Cl\text{-}phen)(bpy)_2^{2+}$ (trace C). All three complexes exhibit a single reversible electrochemical wave over the range examined. Table 2 summarizes the potential for the Ru(II) to Ru(III) oxidation. For each of the complexes, the potential corresponds to oxidation of ruthenium(II) to ruthenium(III). The potentials are $E_{1/2}$ = +1.38 V (trace A), $E_{1/2}$ = +1.34 V (trace B), and $E_{1/2}$ = +1.32 V (trace C). The single wave for each complex

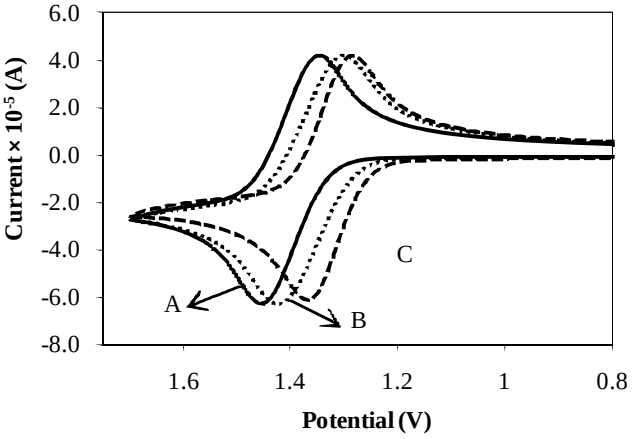


Figure 6. Cyclic voltammograms of the prepared complexes: $Ru(Cl\text{-}phen)_3^{2+}$ (trace A); $Ru(Cl\text{-}phen)_2(bpy)^{2+}$ (trace B); and $Ru(Cl\text{-}phen)(bpy)_2^{2+}$ (trace C).

Table 2. Summary of Ru(II)/Ru(III) redox potentials of the prepared complexes.

Complexes	$E_{1/2}$ (V)
$Ru(Cl\text{-}phen)_3^{2+}$	+1.38
$Ru(Cl\text{-}phen)_2(bpy)^{2+}$	+1.34
$Ru(Cl\text{-}phen)(bpy)_2^{2+}$	+1.32
$Ru(bpy)_3^{2+}$	+1.26
$Ru(phen)_3^{2+}$	+1.26
$Ru(Br\text{-}phen)_3^{2+}$	+1.37

confirms the purity of the prepared complexes. The presence of bpy ligands shifts the wave to lower potentials. This phenomenon indicates the energy of π^* energy levels are lowered by the presence of Cl-phen ligand, and ruthenium complexes with Cl-phen ligands are poor reductants but better oxidants (Rillema et al. 1987).

Conclusions

The present work describes efficient synthetic methods for the preparation of $Ru(Cl\text{-}phen)_3(PF_6)_2$, $Ru(Cl\text{-}phen)_2(bpy)(PF_6)_2$, and $Ru(Cl\text{-}phen)(bpy)_2(PF_6)_2$ complexes. Elemental analysis, mass spectroscopy, and nmr spectroscopy confirm the identity and structural integrity of the prepared complexes. Absorption,emission, and cyclic voltammetric results were very comparable with the reported results for similar compounds. It was observed that the inherently favorable photophysical properties are not substantially altered by the ligand substitution. These complexes are attractive precursors for the construction of high-charge ruthenium complexes by nickel-catalyzed coupling reactions, and presently we are in the process of making the dimer complexes.

Acknowledgments

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